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Heterometallic complex formation on *p*-sulfonatothiacalix[4]arene platform resulting in pH- and redox-modification of $[Ru(bpy)_3]^{2+}$ luminescence

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ABSTRACT

The pH-dependent heterometallic complex formation with *p*-sulfonatothiacalix[4]arene (TCAS) as bridging ligand in aqueous solutions was revealed by the use of spectrophotometry, nuclear magnetic relaxation and fluorimetry methods. The novelty of the structural motif presented is that the appendance of emission metal center ($[Ru(bpy)_3]^{2+}$) is achieved through the cooperative non-covalent interactions with the upper rim of TCAS. The second metal block (Fe(III), Fe(II) and Mn(II)), bound with the lower rim of TCAS in the inner sphere coordination mode is serving as quencher of $[Ru(bpy)_3]^{2+}$ emission. The difference between the complex ability of Fe(III) and Fe(II) ions provides pH conditions for redox-dependent emission of $[Ru(bpy)_3]^{2+}$.

1. Introduction

Ruthenium polypyridyl complexes are of particular importance from the viewpoint of their unique photophysical and photochemical activity [1], which underlay the development of molecular machines and switches [2–6] or mimicking reactions of photosynthesis [7]. Another promising application of ruthenium polypyridyls is caused by their use as building blocks of heterometallic complexes, thus initiating the energy and electron transfer [8–14]. The metal-to-metal energy or photo-induced electron transfer results in quenched luminescence of Ru(II)-containing block in Ru(II)–3d [8–14], or in sensitized lanthanide-centered near infrared luminescence in Ru(II)–4f complexes [15,16]. Though covalent linkage is commonly used to interlock ruthenium polypyridyl block with another metal center via bridging ligand [8–13], the non-covalent binding mode such as ion-pairing between ruthenium tris-bpyridyl and hexacyanates of transition metals is also well known [14]. The use of phenylene bridges is rather common in heterometallic ruthenium containing complexes [9,11–13]. Phenylene bridging ligands provide the possibility of Dexter type energy transfer between metal centers [17]. The work [18] shows the successful use of cyclodextrine as a linkage between ruthenium polypyridyl and dimanganese blocks with photoredox quenching of ruthenium polypyridyl emission. Thus the variation of the bridging ligand structure is of great current interest not only in terms of fundamental studies of energy and electron transfer processes but also due to the potential of multicomponent systems as the basis for molecular devices and electroluminescent displays.

The derivatives of calixarenes are well known as promising platforms for heterometallic complexes, where both metal centers are linked with calixarene through coordination bonds [19,20]. The work [21] provides another example of heterometallic complex, where one of metal centers (lanthanide ion) is inserted into calixarene platform through the inner sphere coordination with donor groups of calixarene substituents, while the second one (ruthenium polypyridyl block) is appended by covalent linkage. It is worth to note that this type of linkage provides the efficient d → f energy transfer. Kitamura et al. showed the way of non-covalent binding of $[Ru(bpy)_3]^{2+}$ block to *p*-sulfonatocalix[4]arene (CAS) through the ion-pairing with its negatively charged upper rim [22]. Later we used the similar binding mode to insert $[Ru(bpy)_3]^{2+}$ to *p*-sulfonatothiacalix[4]arene (TCAS) [23]. The ^1H NMR data in solution and X-ray data in solid state indicate the inclusion of $[Ru(bpy)_3]^{2+}$ into the cavity of TCAS via the fragment of ligand environment. Both CAS and its thia-analogue (TCAS) lead to some quenching of $[Ru(bpy)_3]^{2+}$ emission, which is quite different from the effect provided by *p*-sulfonatocalix[8]arene. According to Shinkai and co-workers [24] the ion-pairing with the latter makes the emission more intensive.

The substitution of methylene bridges on sulfur atoms results in rather striking differences in binding capacity of CAS and TCAS. The

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